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(54) PHOTOPOLYMERIZABLE CONDUCTIVE PASTE COMPOSITION

(57)Abstract:

PURPOSE: To form a thick film fine pattern high in conductivity with a paste containing a metallic powder in high concentration by using a photoradical generator comprising a thioxanthone type dyestuff and amine compound.

CONSTITUTION: This composition is obtained by adding 10-300 pts.wt. of a polyfunctional monomer capable of radical polymerization and 0.1-10 pts.wt. of the photoradical generator to 50 pts.wt. of a binder polymer to impart photosensitivity and mixing 20-500 pts.wt. of the conductive metallic powder with 5 pts.wt. of this photosensitive resin composition. The photoradical generator is composed of the thioxanthone type dyestuff, such as 2,4-diethylthioxanthone or 2,4-dimethylthioxanthone, and the amine compound.

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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] In a photopolymerization nature conductive paste constituent which adds the metal powder 20 - 500 weight sections to photosensitive resin composition 5 weight section which comprises the following (A) (B) (C) 3 ingredient, (C) A photopolymerization nature conductive paste constituent, wherein an optical radical generator which is a component consists of a thioxan ton system pigment and an amine compound.

(A): Binder polymer 50 weight section (B) : the polyfunctional radical polymerization nature monomer 10 - 300 weight sections (C) : the optical radical generator 0.1 - ten weight sections

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is patternized by photoengraving process art, and relates to the photopolymerization nature conductive paste constituent for forming a metal conductor layer according to a subsequent baking process.

[0002]

[Description of the Prior Art] In order to obtain conventionally the thick film insulator, resistor, and conductor layer which were patternized on the high-density multilayered circuit board, Making the nonphotosensitive paste material which mixed inorganic powder to the organic binder patternize on a substrate using printing technique, such as screen-stencil, and dispersing an organic binder according to a subsequent baking process was performed.

[0003] However, in screen printing, it was difficult to form patterns which are stabilized industrially and have the line width of 100 micrometers or less, such as an insulator, a resistor, and a conductor. Near [this] the limit, the platemaking precision of a screen also had the problem of being easy to produce an error bad, and the densification of the pattern was difficult for it. Then, research of the paste which has the photosensitivity which mixed a photosensitive resin composition and inorganic powder for the purpose of acquiring the limit of screen printing for a ***** high-density pattern has been done. The high conductive material paste material of a demand of a circuit pattern

especially detailed also in it is important, and having electrical conductivity with a formed more expensive pattern with formation of a more detailed pattern is called for. . Examination of the photosensitive conductive paste constituent which mixed a photopolymer and metal powder about the conductive material paste composition has been performed. (For example, JP,S54-121967,A, JP,S54-13591,A, JP,S59-143149,A, the European Patent publication of unexamined application No. 414167 Description).

[0004]In order to obtain the metal pattern of high electrical conductivity, high dimensional stability, and low residual carbon quantity, it is necessary to contain metal powder in high concentration. However, by the system which generally contains metal powder, light permeability is low and it is difficult to form a pattern using a photosensitive conductive paste material which made high concentration contain metal powder. For example, in above-mentioned JP,S54-121967,A, JP,S54-13591,A, and JP,S59-143149,A, the system which made metal powder contain most in the description of the embodiment which made metal powder contain was 45 weight %. The polymethylmethacrylate this invention person is also indicated to be to said patent, Although formation of the pattern was tried using photo lithography in the copper paste constituent which 70 weight % of copper powder contains in the photosensitive resin component which consists of a 2 functionality acrylate monomer and a benzyl dimethyl ketal polymerization initiator, The hardenability to the depth direction of an exposure part was insufficient, and formation of the pattern was not completed.

[0005]in the European Patent publication of unexamined application No. 414167 Description, by the description of the embodiment which made copper powder contain 82weight %, although sheet-resistance-values 4mohm/** is obtained by about 10-micrometer thickness, this value remains in the value for the minute of the electrical conductivity of bulk copper half [about]. It thinks it required to make high concentration contain metal powder more, in order for this invention person to get fine PATAON which has still higher electrical conductivity, As shown in comparative example-4, by the photopolymer system similar to the European Patent publication of unexamined application No. 414167 Description, copper powder was made to contain 90weight %, and very high fine pattern creation of electrical conductivity was tried. However, by this system, the formation of the fine pattern was not able to do the contrast of an exposure part and an unexposed part bad.

[0006]

[Problem to be solved by the invention]An object of this invention is to provide the photopolymerization nature paste composition containing metal powder to the high concentration which can form a thick film fine pattern with dramatically high electrical conductivity.

[0007]

[Means for solving problem]Also in the paste which contained metal powder in high concentration dramatically by using the optical radical generator which consists of a thioxan ton system pigment and an amine compound as an optical radical generator as a result of this invention persons' examining a photosensitive resin composition wholeheartedly, It newly found out that formation of the detailed pattern which has the electrical conductivity which is equal to the electrical conductivity of bulk metal was possible, and it was resulted in completion of this invention as a result of research. This invention is based on discovery that the constituent containing the optical radical generator which consists of a thioxan ton system pigment and an amine compound is very effective as photopolymerization nature conductive paste.

[0008]That is, the invention in this application is as follows.

1. In photopolymerization nature conductive paste constituent which adds metal powder 20 - 500 weight sections to photosensitive resin composition 5 weight section which comprises following (A) (B) (C)3 ingredient, (C) A photopolymerization nature conductive paste constituent, wherein the optical radical generator which is a component consists of a thioxan ton system pigment and an amine compound.

Binder polymer 50 weight section (B) : the polyfunctional radical polymerization nature monomer 10 - 300 weight sections (C) : (A): The optical radical generator 0.1 - the photopolymerization nature conductive paste constituent of 10 weight-section this invention. (it is hereafter called a paste composition.) -- even if it sets and contains metal powder in the high concentration of 83 weight % or more, the patternizing by photo lithography is possible. Formation of the metal minute pattern which has very high electrical conductivity in the baking process following exposure and development with this paste material was enabled.

[0009]This invention adds a polyfunctional radical polymerization nature monomer and an optical radical generator to binder polymer, gives photosensitivity, and provides the photopolymerization nature conductive paste constituent which mixed conductive metal powder to the photosensitive resin composition further formed from the above-mentioned compound. The conductor layer which uses metal as a principal component is formed according to the process of exposing and developing this constituent, and the process calcinated after that.

[0010]It becomes a photosensitive resin composition in this invention from three ingredients, binder polymer, a polyfunctional radical polymerization nature monomer, and an optical radical generator. It states in detail below. The binder polymer used for this invention is high-molecular weight corporeal [for forming a polyfunctional radical polymerization nature monomer and interpenetrating network structure], It can use various kinds of high-molecular weight corporeal one, such as acrylic, an amide system, an imide system, a polyalkylene glycol system, a styrene system, an epoxy system, and a polyolefine system. the monomer unit of the ethylenic unsaturated compound which is a polymer formed from one or more sorts of ethylenic unsaturated compounds, and contains one or more carboxyl groups although not limited in particular -- at least 1-mol % -- especially the containing polymer is preferred. Although various kinds of compounds can be used as an ethylenic unsaturated compound, the monomer which forms the polymer in which it depolymerizes or decomposes into easily and carbon and other substances hardly remain with heat is preferred.

[0011]As an example of the monomer unit which can be used for this invention, although various kinds of polymerization nature vinyl monomers can be used, the compound or a cyclic anhydride type compound like maleic anhydride shown by the following-ization 1 can be mentioned.

[0012]

[Chemical formula 1]

[0013]R1, R2, R3, and R4 among [type A hydrogen atom, a halogen atom, A carboxyl group, an ester group, an amino group, an acyl group, an alkoxy group, Low-grade alkyl-group [which was substituted by substituents, such as hydroxyl, an acetoxyl group a low-grade alkyl group, a phenyl group or a halogen atom, a carboxyl group, an ester group, hydroxyl, and an amino group,], or general formula-COOR5, or -CONHR5[R5 among a formula A hydrogen atom, an acyl group, the alkyl group of the carbon numbers 1-18, Or the ester group of an alkyl group, a hydroxy group, an allyl group, an acyl group, The group shown by substitution product [by an ethylene oxide group, carboxylic anhydride groups an acrylic group, a meta-acrylic group, etc.], or formula (CH2-CHR6-O) nR7 (hydrogen and a methyl group, and R7 are an alkyl group of the carbon numbers 1-4, and n= 1-9, as for inside of formula, and R6)] Or the phenyl group substituted by substituents, such as a halogen atom, an alkyl group, a HAROARUKIRU group, a carboxyl group, and hydroxyl, is shown.] The following monomers are mentioned if it is considered as the example. A methylmethacrylate, ethyl methacrylate, butyl methacrylate, Isobutyl methacrylate, lauryl methacrylate, methyl acrylate, Ethyl acrylate, butyl acrylate, stearylacrylate, 2-hydroxy methacrylate, 2-hydroxymethyl methacrylate, Hydroxy propylure methacrylate, hydroxy butyl methacrylate,

Methacrylate, such as glycidyl methacrylate, or acrylate, styrene, chloromethyl styrene, alpha-methylstyrene, hydroxystyrene, ethylene, vinyl chloride, vinyl acetate, etc. can be mentioned.

[0014] Since especially heat decomposability is excellent also in the calcination in a non-oxidizing atmosphere of the polymer which contains a methylmethacrylate, styrene, and alpha-methylstyrene especially among these, it is desirable. Acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, etc. are good as an ethylenic unsaturated compound provided with the carboxyl group which is an example of the unsaturated compound represented with the above-ization 1.

[0015] The substituent which reacts to H₂O or an alkali easily, and generates carboxylic acid and carboxylate, for example, various kinds of carboxylic anhydride groups, reveals the same effect as a carboxyl group. As the example, for example, acrylic acid, methacrylic acid, crotonic acid, The carboxylic anhydride of the ethylenic unsaturated compound which has said carboxyl group produced by making lower-fatty-acid anhydride, lower-fatty-acid halide, etc. react to carboxyl groups, such as itaconic acid, maleic acid, and fumaric acid, can be mentioned. Or cyclic anhydride type compounds, such as maleic anhydride, can be used.

[0016] Although the molecular weight in particular of the binder polymer to be used is not limited, the polymer between 3 million is usually used for a weight average molecular weight (henceforth molecular weight) from 1000. If the low molecular weight polymer whose molecular weight is smaller than 1000 is used, the holdout of conductive powder worsens and is not preferred. If molecular weight exceeds 3 million, the solubility to a solvent and a developer will get worse, and in the creation process and development process of a paste composition, it becomes a problem. desirable -- molecular weight -- the polymer of 10,000 to 3 million -- especially -- desirable -- molecular weight -- the polymer of 60,000 to 1 million -- molecular weight can choose the polymer of 100,000 to 1 million still more preferably. It is desirable in order for using the polymer to which the molecular weight distribution was equal to raise development characteristics.

[0017] In the binder polymer used by this invention, since use of the polymer which has a carboxyl group content monomer unit beyond 1 mol % raises the development characteristics of a minute pattern, it is preferred. The developer used in a development process changes with content of the carboxyl group content monomer unit in binder polymer. although it cannot generally say since the content of the carboxyl group content monomer unit in polymer is based on balance with a radical polymerization nature monomer in order to use a basin system developer -- more than 5 mol % -- desirable -- more than 10 mol % -- it is more than 15 mol % especially preferably. When there is less content of a carboxyl group content monomer unit than 5-mol %, since it becomes refractory to a basin system developer, it is not desirable. moreover -- the case where negatives are developed by a nonpolar organic solvent although it does not limit the maximum in particular of the content of a carboxyl group content monomer unit to in developing negatives by a polar organic solvent -- the content of a carboxyl group content monomer unit -- less than 10 mol % -- it is less than 5 mol % preferably. Since it will become refractory to a nonpolar organic solvent if a carboxyl group content monomer unit contains exceeding 10-mol %, it is not desirable.

[0018] The polyfunctional radical polymerization nature monomer used for this invention is a compound which contains in intramolecular two or more functional groups which carry out a radical polymerization reaction according to an operation of an optical radical generator. For example, the compound which contains an acrylic group, an methacrylic group, an acrylamide group, maleic acid Oertel, an allyl group, vinyl ether, a vinylamino group, an acetylene nature unsaturated group, etc. in intramolecular can be mentioned. These compounds carry out a polymerization reaction according to an operation of an optical radical generator, and form the polymerization constituent which gels by forming said binder polymer and interpenetrating network structure, and becomes insoluble at a developer.

[0019] Although the monomer which carries out a radical reaction can use various kinds of compounds, since it tends to gel polymerization nature highly, polyfunctional acrylate or especially a polyfunctional methacrylate monomer is preferred. For example, diethylene glycol diacrylate, triethylene glycol diacrylate, Polyethylene glycol diacrylate, such as tetraethylene glycol diacrylate, Or the methacrylate corresponding to polyurethane diacrylate, it, etc., Pentaerythritol bird acrylate, trimethylolpropane triacrylate, Trimethylolmethane bird acrylate, the ethylene oxide denaturation trimethylolpropane triacrylate which showed structure to ** 2, The propylene oxide denaturation trimethylolpropane triacrylate which showed structure to ** 3, The epichlorohydrin denaturation trimethylolpropane triacrylate which showed structure to ** 4, Pentaerythritol tetraacrylate, pentaerythritol tetra methacrylate, Tetramethylolmethane tetraacrylate, the ethylene oxide denaturation phosphoric acid bird acrylate which showed structure to ** 5, the epichlorohydrin denaturation glycerol bird acrylate which showed structure to ** 6, dipentaerythritol hexaacrylate, The methacrylate monomer corresponding to polyfunctional acrylate or it etc. which is represented by dipentaerythritolmonohydroxypentaacrylate etc. can be chosen. The polyfunctional acrylate which made carboxyl group containing polymer, such as polymethacrylic acid, polyacrylic acid, and polymaleic acid, esterify and carry out the amidation reaction of butanediol monoacrylate, the polyethylene glycol acrylate, etc., and introduced the acrylate group into it can be used.

[0020] The photopolymerization nature conductive paste constituent with high photopolymerization sensitivity was especially obtained by the system using two organic functions, three organic functions, and 4 organic-functions monomer. These polyfunctional RAJIRARU polymerization nature monomers may be independent, or may be mixtures. The monofunctional monomer may be contained in the photosensitive resin composition in this invention. the content -- 50 or less weight % of the polyfunctional radical polymerization nature monomer whole quantity -- desirable -- 30 or less weight % -- it is . If a monofunctional monomer is made to contain exceeding 50 weight sections, it is not desirable in order for it to become insufficient forming of interpenetrating network structure with the polymer of the exposure part of a paste composition and to bring about the fall of gelling.

[0021]

[Chemical formula 2]

[0022]

[Chemical formula 3]

[0023]

[Chemical formula 4]

[0024]

[Chemical formula 5]

[0025]

[Chemical formula 6]

[0026] The optical radical generator of this invention consists of a thioxan ton system pigment and an amine compound, and carries out 0.1-10 weight-section addition to binder polymer (A) 50 weight

section. The photo-setting nature of a paste composition is not low more preferred in the loadings of few optical radical generators than in 0.1 weight sections. Even if it adds exceeding ten weight sections, since the improvement in photo-setting nature is not found but reduces hardenability conversely, it is not preferred. The thioxan ton system pigment used as an optical radical generator of this invention is a compound which has thioxan ton structure in intramolecular, for example, the compound shown by the following-ization 7 can be used. Also in the compound concerned, for example, 2, 4-diethylthio xanthone, 2, 4-dimethyl thioxan ton, The derivatives, such as 2-KURORU thioxan ton, 2-methyl thioxan ton, isopropyl thioxan ton, 2, 4-dichloro thioxan ton, 2, and 4-dipropyl thioxan ton, can be mentioned. It can use as independent [these] or two or more sorts of mixtures.

[0027]

[Chemical formula 7]

[0028]the inside of a formula, R1, R2, R3, and R4 -- a hydrogen atom and a halogen atom. A carboxyl group, an ester group, an acyl group, an alkoxy group, hydroxyl, An acetoxo group, a low-grade alkyl group or a halogen atom, a carboxyl group, The low-grade alkyl group substituted by substituents, such as an ester group, hydroxyl, an amino group, and a phenyl group, is shown. Aliphatic series and aromatic amine are used again as an amine compound which is an essential ingredient used in combination with a thioxan ton system pigment. For example, triethylenetetramine, triethanolamine, methyldiethanolamine, Tri-isopropanolamine, n-butylamine, N-methyldiethanolamine, Diethylamino ethyl methacrylate, 4, and 4'-dimethylamino benzophenone, 4 and 4'-diethylamino FENON, 4, and 4'-diethylamino benzophenone, 4-dimethylamino ethyl benzoate, 4-dimethylaminobenzoic acid (n-butoxy) ethyl, 4-dimethylamino isoamyl benzoate, etc. can be mentioned. Aromatic amines, such as 4,4'-dimethylamino benzophenone, 4,4'-diethylamino FENON, 4-dimethylamino ethyl benzoate, 4-dimethylaminobenzoic acid (n-butoxy) ethyl, and 4-dimethylamino isoamyl benzoate, are especially preferred. An amine compound can be preferably added in the range of 0.5 to 5 weight section 0.1 to 10 weight section to thioxan ton system pigment 1 weight section. Since the addition of those other than a mentioned range does not contribute to improvement in the photo-setting nature of a paste composition, it is not preferred.

[0029]The rate of binder polymer in the photosensitive resin composition used for this invention and a polyfunctional radical polymerization nature monomer is important for the pattern formation characteristics of a photopolymerization nature conductive paste constituent. As for each rate, it is desirable that it is in the next range.

Binder polymer: 50 weight-section polyfunctional radical polymerization nature monomer : If a 10 - 300 weight-section polyfunctional radical polymerization nature monomer exceeds 300 weight sections, it will become difficult to maintain viscosity good as a paste composition. The pattern formation nature in exposure and a development process worsens, and is not preferred. If a polyfunctional radical polymerization nature monomer will be ten or less weight sections, the soluble difference in the development process of an exposure part and an unexposed part will decrease, pattern formation nature gets worse, and it is not desirable. The polyfunctional radical polymerization nature monomer of 30 to 80 weight section is more preferably added to binder polymer 20 to 100 weight section.

[0030]The rust-proofer for preventing thermal-polymerization inhibitor, a solvent, and scaling if needed, etc. can be added. As thermal-polymerization inhibitor, salts, such as the hydroquinone usually known, methylhydroquinone, t-butyl catechol, pyrogallol, phenol and its derivative, copper, or iron, etc. can be used. About 0.01-1 weight section of the amount used can suppress a thermal polymerization, if it adds to the photosensitive resin composition 100.

[0031]Glass frit etc. can be added in order to raise an adhesive property with the substrate after calcination. It is preferred to use 5 or less weight % of metal powder as the loadings. Since it will

become the cause of reducing the electrical conductivity after calcination if it adds exceeding 10 weight %, it is not desirable. It carries out for accumulating and addition of a solvent has [which adjusts paste viscosity when applying the photopolymerization nature conductive paste constituent of this invention on a substrate / a 60-260 ** thing] good operativity as a boiling point of a solvent. That [60 ** or less] also has high *****, and brings about high viscosity-ization at the time of paste kneading, and there is a problem of reducing preservation stability. If a not less than 260 ** thing is used, drying will become insufficient, and it becomes difficult to make it stick to a mask surface at the time of exposure. As a suitable solvent, for example, n-methyl pyrrolidone, ethylene glycol monoethyl ether, There are an aromatic compound of high-boiling points, such as a derivative of the polyhydric alcohol of high-boiling points, such as ethylene glycol monobutyl ether and ethylene glycol monoethyl ether acetate, and xylene, ketone, ester species, and terpenes.

[0032]In this invention, metal independent, such as gold, silver, platinum, palladium, copper, an aluminium, nickel, and tungsten, or after alloy powder, the metal powder that covered the surface with other metal, etc. can be used as metal powder. The copper powder which gold, silver, platinum, palladium, and copper were independent, or was especially covered with noble metals, such as after alloy powder or gold, silver, platinum, and palladium, can use preferably.

[0033]The surface of copper system metal powder with a small grain size oxidizes easily, and there are many oxygen contents in metal. When powder with many oxygen contents is used, there is a case where the viscosity of a paste increases during paste adjustment or preservation, and it becomes impossible to hold a paste state. In order to avoid such a problem, it is effective that the oxygen content in the powder by surface oxidation uses 0.2 or less weight % of metal powder more preferably 0.5weight % 2 or less weight %. In order to obtain the less metal powder of an oxygen content, the reduction treatment of the surface oxide layer by calcination by a reducing gas atmosphere is effective.

[0034]Metal powder can choose the rate of metal powder and a photosensitive resin composition in the range of 25 to 95 weight section more preferably 25 to 300 weight section 20 to 500 weight section to total quantity 5 weight section of a photosensitive resin composition. When the rate of metal powder is 20 or less weight sections, since pack density is not enough, the conductor layer which has electrical conductivity high like metal powder does not sinter well but they are equal to the electrical conductivity of bulk metal at the time of calcination, and has sufficient hardness cannot be formed. Since an organic substance component cannot be dispersed enough and a film with much residual carbon quantity is formed, it is not desirable. Since volume shrinkage becomes remarkable in a baking process, the problem to which dimensional stability falls is also produced. If the rate of metal powder exceeds 500 weight sections, since there is too little content of a photosensitive resin composition, formation of a pattern cannot be performed.

[0035]The shape of metal powder can use the thing of arbitrary shape, such as a globular shape, a column, and a thin film integrated circuit. Although a powdered grain size changes with the sizes and thickness of a pattern of a conductor layer to form, When forming a pattern with a line width of about 100 micrometers generally, can use a thing with a grain size of 50 micrometers or less, but. In order to obtain the pattern especially whose line width is about 50 micrometers, the thing of the range of 0.01-10 micrometers is usually used, and, as for the grain size of the powder to be used, the thing of the range of 0.1-10 micrometers is used preferably. moreover -- although a grain size can also use the powder distributed over this range -- a grain with a grain size of 0.4-5 micrometers -- more than 80wt% -- use of the powder to contain is preferred. When grains smaller than 0.01 micrometer are used, base metal, such as copper, becomes difficult [it / to form a conductive high pattern that it is very easy to oxidize]. The resolution of a pattern is low when bigger grains than 20 micrometers are used, in order to obtain an about 50-micrometer pattern. The powder which performed a surface treatment, such as carrying out the coat of the metal powder of a copper system in which the surface oxidizes easily by polymer etc., can also be used.

[0036]Spreading to the substrate of the photopolymerization nature conductive paste constituent of this invention can be performed by the usual method of having used screen-stencil, a roll coater, or a doctor blade. Although the thickness in particular of the paste composition applied on a substrate does not limit, in order to obtain an about 50-micrometer pattern, it is preferred to use 50 micrometers or less.

[0037]A photopolymerization nature conductive paste composition is applied to a substrate, and it exposes after desiccation using a near-ultraviolet light line or an ultraviolet radiation line. Since it is preferred to use for the wave range of a near ultraviolet ray or an ultraviolet region the compound which has spectral sensitivity as an optical radical generator when adjustment of a photopolymerization nature conductive paste constituent and the operativity of a patternizing process are taken into consideration, it is more preferred than 450 nm to use the light source which the light by the side of short wavelength generates. For example, light sources, such as a laser which generates the light of an ultrahigh pressure mercury lamp, a high pressure mercury vapor lamp, a xenon lamp, or this wave range, can be used.

[0038]When carboxyl group containing binder polymer is used also in the binder polymer used by this invention, the dispersibility of the metal powder in the inside of a photosensitive resin composition is very high. Therefore, when negatives are developed with a basin system developer or an organic solvent system developer after exposure, Also in the constituent which began to get loose out of the system in the shape of a particle, and moreover contained metal powder in high concentration, the velocity of the metal powder of an unexposed part which begins to get loose is very early, Development characteristics outstanding farther than the case where the conventional photosensitive resin composition which uses the binder polymer which does not contain the carboxyl group is developed with an organic solvent are shown in a photosensitive resin composition.

[0039]As a basin system developer, a weak-alkaline-water solution is preferred. As an example of an alkali developing solution, sodium carbonate, sodium hydroxide, Organic alkali aqueous solutions, such as organic amine, such as inorganic alkali, such as potassium hydroxide and ammonia, and hydroxy trimethylammonium, 2-hydroxyethyl trimethylammonium, and ethanolamine, can be used. The concentration of an alkaline aqueous solution is 2 or less weight % of 0.3 weight % or more 5 or less weight % of 0.1 weight % or more preferably. Even if it uses a high-concentration alkaline aqueous solution from 5 weight %, since development velocity becomes slow when it does not improve and an aqueous solution thinner than 0.1 weight % is used, development velocity is not preferred. After making an unexposed part eluted by an alkaline aqueous solution, a rinse distance excluding an excessive alkali solution using water is effective.

[0040]It can be used if it is a solvent which dissolves the photosensitive resin composition used by this invention as an organic solvent system developer. As a developing method used by this invention, it can use with the usual method. For example, the dip method dipped into a developer, the spray method which sprays a developer, etc. can be mentioned. In particular, for minute pattern formation, the spray developing-negatives method is very effective.

[0041]pass the process of calcinating the paste composition pattern formed of the development process, in this invention -- high metal pattern **** of electrical conductivity -- things are made. The above-mentioned process of calcinating means the process which disperses the photosensitive resin composition in a paste composition, and makes metal powder sinter. In the case of the metal of a copper system which oxidizes easily, calcination in a non-oxidizing atmosphere is preferred. Inert gas, such as nitrogen, helium, argon, and neon, can be used, and it is necessary to keep desirable 100 ppm or less of oxygen concentration at 50 ppm or less as gas for forming a non-oxidizing atmosphere. In the case of the metal which oxidizes easily, mixed gas with reducing gas, such as hydrogen and carbon monoxide, or the aforementioned inert gas, etc. can be used. Although a burning temperature changes with kinds of photosensitive resin composition to be used, in order to

disperse an organic ingredient, it is necessary to make it into the temperature more than the decomposition temperature of a photosensitive resin composition at least. Since metal powder sinters by carrying out more than the sintering temperature of the metal currently used, the conductor layer which has high electrical conductivity can be obtained. therefore -- although a burning temperature changes with kinds of a photosensitive resin composition or metal -- usually -- the range of 300-1200 ** -- the range of 400-1000 ** is used preferably.

[0042]

[Working example] Although the following embodiments and comparative examples explain this invention concretely, it is not limited to this. The weight average molecular weight shown in the following embodiments was measured using the following GPC (gel permeation chromatography).

GPC: Jasco make (pump: the calibration curve was prepared by TRI ROTAR-V, column: Shodex A-800P (precolumn), A-80Mx2 series, eluate: THF, and a standard polystyrene sample, and the weight average molecular weight was measured.),

[0043]

[Work example 1] As opposed to binder polymer 50 weight section of the molecular weight 130,000 which consists of 25 mol of methacrylic acid %, and butyl acrylate 10 mol % methylmethacrylate 65 mol%, Ethylene oxide denaturation TORIMERI roll propane acrylate 50 weight section shown in the following-ization 8, 2, 4-diethylthio xanthone 1.5 weight section, 4-dimethylamino ethyl benzoate 3.5 weight section, and n-methyl-pyrrolidone 135 weight section were stirred, and the photosensitive resin composition was obtained.

[0044]

[Chemical formula 8]

[0045] To this photosensitive resin composition 5 weight section, copper powder 45 weight section with a mean particle diameter of 3 micrometers was kneaded by 3 roll mills, and the photopolymerization nature conductive paste constituent was obtained. The oxygen concentration in the used copper powder is an oxygen and nitrogen simultaneous analysis device. As a result of measuring made in Horiba Work Place and using [EMGA-650 type], it was 0.15 weight %. On the alumina-ceramics board, the roll coater was used, this paste composition was applied, and it dried in 70 ** oven. The thickness after desiccation was 20 micrometers. Next, it irradiated with the light of 250W ultrahigh pressure mercury lamp for 600 seconds under a nitrogen atmosphere via the mask for exposure, and heat-treated at 70 ** for 15 minutes. Then, spray development was carried out by using a sodium carbonate aqueous solution as a developer 1 weight %. The photomask used for formation of a pattern was shown in drawing 1. In this pattern, it has patternized to the thing with a line width of 40 micrometers. This was held at 500 ** under a nitrogen atmosphere for 1 hour, and it calcinated for 30 minutes at 900 more **. The thickness of the pattern remaining on the substrate is 15 micrometers, and has the gloss of metallic copper. When the line width of 1 mm, 40 mm in length, and the line pattern of 13 micrometers of thickness after calcination were formed and volume resistivity was measured like the above-mentioned method, it was 2.6 micro ohm-cm. This was a value near 1.7 micro ohm-cm which is the volume resistivity of metallic copper.

[0046]

[Work example 2] As opposed to binder polymer 50 weight section of the molecular weight 110,000 which consists of 5 mol of methacrylic acid % methylmethacrylate 95 mol%, The photosensitive resin composition was obtained by stirring pentaerythritol bird acrylate 100 weight section, isopropyl thioxan ton 3 weight section, 4-dimethylamino ethyl benzoate 10 weight section, and ethylene-glycol-monoethyl-ether 130 weight section. To this resin composition 5 weight section, copper powder 25 weight section with a mean particle diameter of 2 micrometers was kneaded using

3 roll mills, and the photopolymerization nature conductive paste constituent was created. The oxygen content of the used copper powder was 0.1 weight %, as a result of measuring using the same device as Embodiment 1. This paste composition was applied on the ceramics board on the whole surface using the roll coater, and a 25-micrometer film was obtained after desiccation at 70 **. It exposed under the nitrogen atmosphere of 3 to 5% of oxygen concentration through the photomask for 600 seconds with 250W ultrahigh pressure mercury lamp which is an ultraviolet ray source after that, and the latent image was formed. Furthermore, this was developed by the spray developing-negatives method by using 1, 1, and 1-trichloroethane as a developer. As a result of forming an image using the photomask shown in drawing 1, even a 40-micrometer pattern has been developed. Furthermore, it held for 60 minutes at 400 ** under a nitrogen atmosphere, and the organic binder component was removed, by subsequently carrying out temperature up to 850 **, grains were made to sinter and the conductor layer of 3.2micro of volume resistivity ohm-cm which has metallic copper gloss was obtained.

[0047]

[Work example 3]To photosensitive resin composition 5 weight section of the same presentation as Embodiment 1, copper powder 95 weight section with a mean particle diameter of 3 micrometers of 0.08 weight % of oxygen concentration was kneaded using 3 roll mills, and the photopolymerization nature conductive paste constituent was obtained. It applied by 10-micrometer thickness on the ceramics board on the whole surface using the roll coater. Exposure, development, and calcination were performed by the same method as Embodiment 1. As a result, a 60-micrometer pattern was able to be obtained in the photomask pattern shown in drawing 1.

[0048]

[Embodiments 4-6] To the sensitization Naruki fat constituent 5 same weight section as Embodiment 1, alloy (content of palladium was 30 weight %.) 25 weight section of gold with a mean particle diameter of 1-5 micrometers, silver, and palladium and silver was mixed using 3 roll mills, and the photopolymerization nature conductive paste constituent was obtained. These paste compositions were applied on the ceramics board by 15-micrometer thickness. In any case, the oxygen content of these exotic powdered metals was 0.1 or less weight %. By the same method as Embodiment 1, exposure and development were performed and formation of a 60-micrometer pattern was checked in said photomask pattern.

[0049]

[Work example 7]the copolymer (the Monsanto Co. make.) of styrene and maleic acid monoester A trade name and Scripset550 were able to be used as binder polymer, copper powder with a mean particle diameter of 3 micrometers was able to be made into 25 weight sections, and 15 micrometers of thickness and a metallic copper pattern with a line width of 80 micrometers were able to be obtained like Embodiment 1 except exposing under the nitrogen atmosphere of 3 to 5% of oxygen concentration.

[0050]

[Work example 8]The ethylene oxide denaturation TORIMERI roll propane acrylate shown by the above-ization 8 was made into 30 weight sections, except making copper powder of the mean particle diameter of 3 micrometers, and 0.08 weight % of oxygen content into 20 weight sections, the photopolymerization nature conductive paste constituent was created on the same conditions as Embodiment 1, and the metallic copper pattern was formed. As a result, 10 micrometers of thickness and a copper pattern with a line width of 60 micrometers were obtained.

[0051]

[Work example 9]The ethylene oxide denaturation TORIMERI roll propane acrylate shown by the above-ization 8 was made into 80 weight sections, except making copper powder of the mean particle diameter of 3 micrometers, and 0.08 weight % of oxygen content into 25 weight sections, the photopolymerization nature conductive paste constituent was created like Embodiment 1, and

the metallic copper pattern was formed. As a result, 10 micrometers of thickness and a copper pattern with a line width of 60 micrometers were obtained.

[0052]

[Work example 10]As binder polymer, 3 mol of maleic anhydride %, styrene 3 mol %, 20 micrometers of thickness and a copper pattern with a line width of 60 micrometers were obtained like Embodiment 2 using the copper powder of the mean particle diameter of 3 micrometers, and 0.08 weight % of oxygen content except using the Kolin aqueous solution 1weight % as a developer, using the copolymer which consists of 94 mol of methyl methacrylate %.

[0053]

[Work example 11]The pattern with a line width of 60 micrometers was able to be formed like Embodiment 2 except adding silicon-oxide-zinc oxide-lead-oxide system glass frit 1 weight section whose mean particle diameter is 2 micrometers, using the polymethylmethacrylate of the molecular weight 360,000 as binder polymer.

[0054]

[Work example 12]To the photosensitive resin composition 5 same weight section as Embodiment 1, the grain size was distributed over 0.2-4 micrometers, and mixed copper powder 45 weight section whose mean particle diameter is 2 micrometers using 3 roll mills under a nitrogen atmosphere with an oxygen concentration of 10 ppm or less, and the photopolymerization nature conductive paste constituent was obtained. The obtained paste composition was applied on the alumina substrate by 15-micrometer thickness. The oxygen content of the used copper powder was 0.1 or less weight %. Exposure and development were performed by the same method as Embodiment 1, and formation of a 40-micrometer pattern with little ANDAKATTO was checked in said photomask pattern. The volume resistivity of the metallic copper thin film obtained after calcination was 2micro ohm-cm.

[0055]

[Comparative example 1] Although pattern formation was tried like Embodiment 2 except using the polymethylmethacrylate of the molecular weight 200,000 as binder polymer, and using benzyl dimethyl ketal as an optical radical generator, the pattern after spray development did not remain.

[0056]

[Comparative example 2] Although formation of the pattern was tried like Embodiment 1 except using benzyl 1.5 weight section and 4 and 4'-dimethylamino ethyl benzoate 3.5 weight section as an optical radical generator, Only the very large things of the defect were obtained also in the pattern whose surface photo-setting nature is the line width of 200 micrometers bad.

[0057]

[Comparative example 3] as an optical radical generator -- 2-methyl-1-(4-methyl thiophenyl)-2-morpholino propane- 1-ON (the Ciba-Geigy make.) Although patternizing was tried like Embodiment 2 except using the polymethylmethacrylate of the molecular weight 200,000 for Irgacure907 1.5 weight section and 4 and 4'-dimethylamino ethyl benzoate 3.5 weight section as binder polymer, Formation of the pattern with a line width of 200 micrometers or less was not completed.

[0058]

[Comparative example-4] Formation of the pattern was tried like Embodiment 1 except using benzophenone 5 weight section and Michler's ketone 0.8 weight section as an optical radical generator. As a result, since the solubility of an unexposed part was remarkable and bad, only the pattern in which the contrast of an exposure part and an unexposed part is very low was obtained, and the fine pattern with clear edge was not obtained. .

[0059]

[Effect of the Invention]By using the photopolymerization nature conductive paste constituent of this invention, it became possible by the conventional paste to obtain the thick film fine pattern which has the impossible high conductivity.

[0060]

[Translation done.]